

고온에서 형성된 하이드로탈사이트 결정구조의 물성특성 연구

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(mhk22@cam.ac.uk, myunghunkim@ymail.com*)**The Study on the Physical Properties of Crystal Structure Hydrotalcite formed at High Temperature**Myung Hun Kim*, Seok-Heung Jang¹, Seon Nam Kim²

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Introduction

Hydrotalcite, magnesium-aluminum hydroxycarbonate, has a layered crystal structure of chemical composition $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ comprising of positively charged hydroxide layers and interlayer composed of carbonate anions and water molecules [1]. The ordering of hydroxide layers is similar to brucite, $Mg(OH)_2$, where each Mg^{2+} cation is octahedral $[Mg(OH)_6]^{4+}$ share edges to form infinite sheet. In the hydrotalcite, Mg^{2+}/Al^{3+} isomorphous substitution in octahedral sites of the hydroxide sheet results in a net positive charge, which has to be neutralized by interlayer anionic species [2].

A large number of studies on physical-chemical properties and application of hydrotalcite-like compounds was reported, but only a few reports discussed the control of particle size, which is an important parameter in industrial applications [3]. In many cases, an optimization of experimental conditions for particle size growth could not be described well for a well-crystallized hydrotalcite-like phase transformation.

The hydrothermal treatment was used in order to improve the crystalline of various layer double hydroxides such as Ni-Al, Ni-Cr [4]. The crystallinity of $Mg-M^{III}$ compounds ($M^{III} = Al, Cr, Fe$) was also enhanced by the microwave irradiation [5]. Hickey et al. studied the influence of hydrothermal treatment on the crystallinity of hydrotalcite [6]. Especially, the temperatures play important roles in crystallization and crystal growth owing to can obtain crystalline particle of a definite hexagonal morphology by hydrothermal treatment.

In general, synthesized hydrotalcites from the low temperature by co-precipitation method showed the agglomeration of small crystals and difficult to the control of regular particle sizes but hydrotalcites by hydrothermal treatment at the high temperature with time control showed an increasing growth of crystallites as well as an improvement of the crystalline.

An improvement of the crystallinity for hydrotalcite may be achieved by temperature and time under hydrothermal condition. The crystallization was usually carried out at temperatures range from RT to 200 °C under autogenously pressure for a time ranging from some hours to days. In this study, the hydrotalcite with $Mg/Al=3.0$ was synthesized under hydrothermal conditions at various temperatures in the range from RT to 180 °C for 12 hr - 48 hr in time. The obtained samples were characterized using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) for crystallinity.

Experimental

Hydrotalcite samples are prepared by the co-precipitation method at constant pH 9.5-10.0. Typically, 200ml of an aqueous solution A containing 19.4g $Mg(NO_3)_2 \cdot 6H_2O$ and 9.6g $Al(NO_3)_3 \cdot 9H_2O$ and 200ml aqueous solution B consisting of 8.2g NaOH and 2.6g anhydrous Na_2CO_3 were added simultaneously in the reactor a four neck round flask (1000ml) and then hydrothermally treated in the autoclave from RT to 180 °C for 12 hr - 48 hr. Finally, we are obtained the solid products by centrifugation and freezing dry.

Results and Discussion

The XRD patterns of solid product obtained from the room temperature (RT) and hydrothermal treatments are shown in Fig. 1. In the hydrothermal treatment, an increasing intensity of diffraction lines were appeared with increased temperature, particularly at 180 °C temperature for 48 hrs. The integral intensities of both (003) and (006) reflections are distinctly observed to sample treated hydrothermal than co-precipitated product. This means the crystallinity formation through crystal growth of hydrotalcite with the temperature increase through (003) and (006) peaks. Therefore, temperature and time are seems to be a crucial parameter affecting crystallization of particles under hydrothermal condition. The morphologies of co-precipitation and hydrothermal treated samples

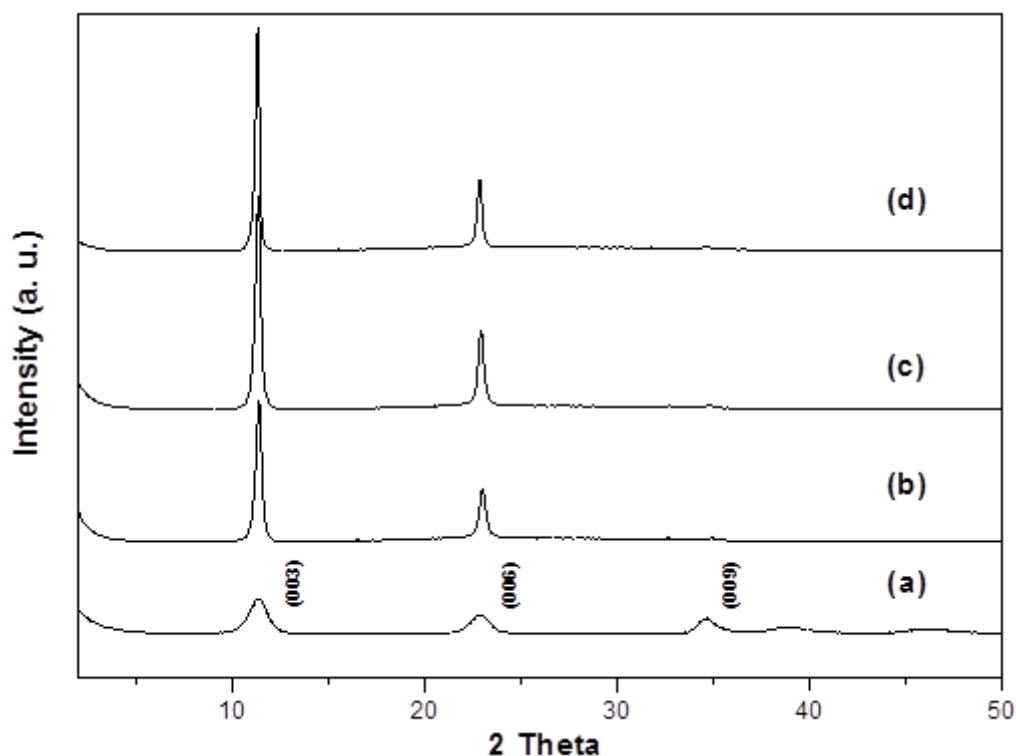


Fig. 1. Powder X-ray diffraction patterns of hydrotalcite samples: (a) RT, (b) 160 °C, 48hr, (c) 170 °C, 48hr, (d) 180 °C, 48hr.

were observed by scanning electron microscope (SEM), as shown in Fig. 2. SEM image of (a) is hydrotalcite prepared by co-precipitation in RT and (b), (c) and (d) are samples treated a high temperature 160, 170 and 180 °C for 48 hr, respectively. As can be seen in this figure, the results are significantly different, in particular, in particle shape, that Fig. 2a is not definite crystal phase by the agglomeration of small crystals but shown a distinct difference the crystal phase of hexagonal morphology with increasing the temperature in Fig. 2d. In other words, SEM image showed a gradual crystallization of hydrotalcite and a change of crystal size by the increase of the temperature and became sufficient evidence the crystallinity through crystal growth of hydrotalcite. These results agree with intensity increase at (003) and (006) in XRD.

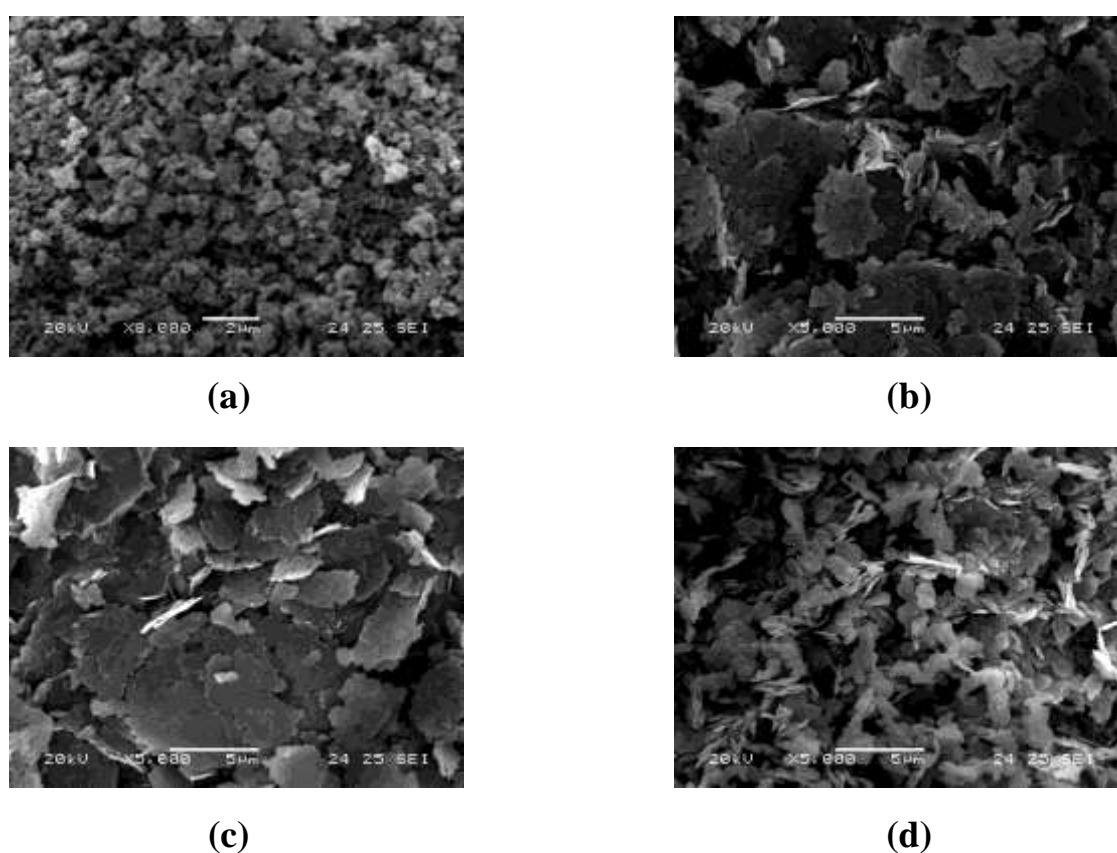


Fig. 2. SEM image of hydrotalcite samples synthesized at the room temperature and hydrothermal treated a high temperature: (a) RT, (b) 160 °C, 48hr, (c) 170 °C, 48hr, (d) 180 °C, 48hr.

Conclusion

Several conclusions have been drawn through this study. First of all, the results suggest that hydrothermal synthesis would be highly effective for the crystallization of hydrotalcite regarding crystallization temperature and time compared to co-precipitation, that is, hydrotalcite with crystallinity with hexagonal morphology could be synthesized within 48 hrs through hydrothermal

synthesis .

Second, it is seen that the effect of stirring on the temperature, time and morphology seems to be significant. It might be attributed to the difference in crystallisation that the largest activation energy for nucleation stage of crystal growth formation and transition and crystallization stages, suggest that nucleation stage should be an energetically activated process and a rate-limiting step with temperature and time. Furthermore, this study suggests that the most important parameter of crystallinity is temperature and time affecting the hydrothermal crystallization and could be explained for the increase of hydrotalcite crystal size using above-mentioned parameters.

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